

25p.

N 64 13187A

CODE-1

CR-~~55212~~



OTS PRICE

XEROX	\$	<u>2.60 ph.</u>
MICROFILM	\$	<u>0.95 mf.</u>

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

RE-ORDER NO. 63-467

(NASA-CR-55217

AI-8971

OTS: \$2.60 ph
\$0.95 mf

RADIATION EFFECTS ON
ELECTRODE BEHAVIOR

Midpoint Report,
31 Jun - 31 August 1963

per
G. R. Argue,
H. L. Recht, and
W. A. McCollum Pasadena, Calif., Jet Propulsion Lab., 1963

25p *(Oufs)*

☒ OTS
☐ 2
This work was performed for the Jet Propulsion Laboratory,
California Institute of Technology, sponsored by the
National Aeronautics and Space Administration under
Contract NAS7-100.

→ (NASA Contract NAS7-100;
JPL Contract 950514)

0929000

~~(WATER-100)~~ index or JPL-950514

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: 950514 AISO No. 2469
ISSUED: September, 1963
REVISED: October 14, 1963

TABLE OF CONTENTS

	Page
I. Summary	1
II. Introduction	2
III. Factual Data	3
A. Preliminary Tests	6
B. Irradiation Tests	7
C. Temperature Characteristics of Ni-Cd Batteries17
IV. Discussion and Conclusions20
V. Plans for Further Work21

I. SUMMARY

13/87

Equipment and circuitry were assembled to provide either manual or automatic cycling of the nickel-cadmium cells through charge and discharge cycles. Quartz cells were designed and constructed for use in the Co^{60} (gamma) and SNAP STF (neutron) sources. Laboratory experiments were carried out to determine the capacity, elevated temperature characteristics, and the general electrochemical behavior of 2-electrode cells under various current cycling regimes. These cells used electrodes taken from Gulton VO series Ni-Cd cells. Gamma irradiation runs have been carried out at the NAA Science Center Co^{60} source (dose rate = 1.9×10^6 rads/hr) and at the AI Co^{60} source (dr = 8×10^4 rads/hr). A small deterioration in output voltage with time (of the order of tens of millivolts) was observed at dosages of 10^8 rads, but the results were clouded by having to correct for the effects of a simultaneous high temperature produced in the source to obtain this figure. Sloughing off of electrode material, almost entirely from the cadmium (negative) electrode became apparent at about 6×10^6 rads. At 1.3×10^7 rads, or some lesser figure, the capacity of the cadmium electrode is drastically reduced. Some possible mechanisms for this damage are presented. The future program of irradiations, to include neutron and electron sources, also calls for chemical tests to pinpoint or eliminate H_2O_2 as the primary cause of this material loss.

AUT 402

II. INTRODUCTION

The objective of this program is to investigate the effects of irradiation, neutron and gamma, on the characteristics and properties of nickel-cadmium battery electrodes. The effects are to be looked for specifically by monitoring the electrochemical characteristics of a battery during charge and discharge cycles both in and out of radiation fields. Along with the electrical measurements, any physical changes are to be noted, studied, and their effect correlated to the electrochemistry of the system. Temperature and pressure measurements are to be monitored and their variances studied.

To date, all irradiations have involved gamma sources, although neutron irradiation is planned for the next period. Two significant results have shown up. First, a small drop in cell voltage (at open circuit and during charge-discharge cycling) was observed. Of the order of tens of millivolts, the effect appears to be a function of integrated dose. Determination of the magnitude of the effect was difficult as the value had to be corrected for simultaneous decrease in output voltage caused by the elevated temperature encountered. However, while the exact value of this effect is in doubt, its existence appears confirmed.

A second, more striking effect was observed. The electrodes, in particular the cadmium (negative) electrode, was observed to disintegrate, so that a noticeable deposit appeared after about 6×10^6 rads integrated dosage. This phenomenon seems to have little effect on the cell voltage but appears to have some effect on the total capacity. This phenomenon was studied rather thoroughly. The first phase of this study was the determination of the time for appearance of the deposits and the effect of dose rate on this

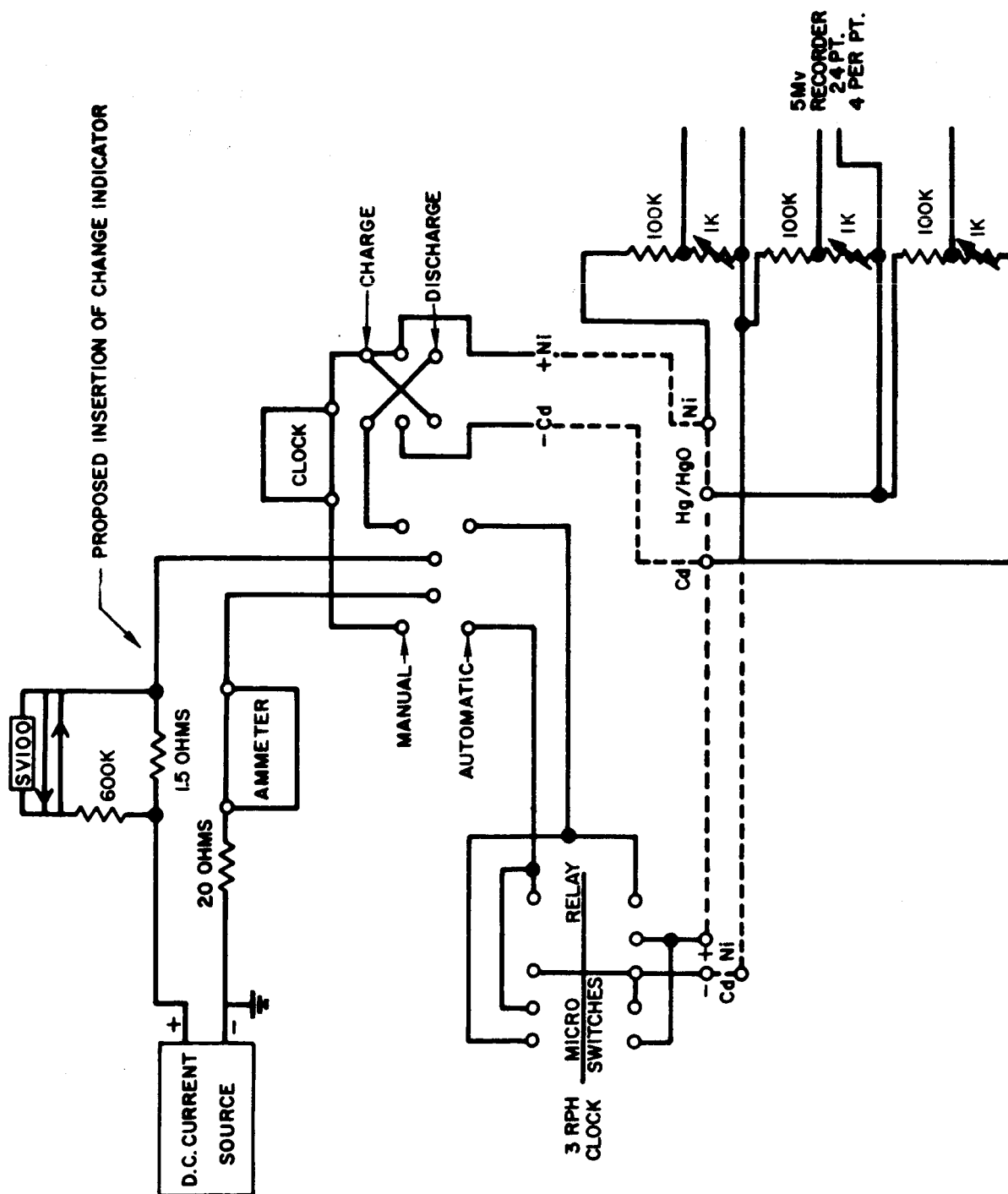
time and the phenomenon itself. The second phase would be to see what effect this sloughing off of material had on the charge-discharge curves of the cells. This second phase has not been initiated as yet.

III. FACTUAL DATA

Equipment to be used, including multipoint recorder, constant current source, timer and a multicam clock assembly, were assembled in a portable rack so that two cells with reference electrodes (Hg/HgO) can be monitored during a complete cycle. The cycle selected for this initial work is of 20 minute duration; 6 min charge, 4 min open circuit, 6 min discharge, 4 min open. During the period the voltages between the Ni-Cd, Ni-Hg/HgO and Cd-Hg/HgO are monitored five times per minute. The circuitry for this system is shown in Figure 1.

Since laboratory studies on the normal characteristics of the batteries were needed along with the irradiation studies, two types of cells were designed. The laboratory cell is a two compartment lucite box with an air tight top. Electrodes and pressure measuring devices are sealed in. With this system the cells can be dismantled easily.

For irradiation, quartz cells were constructed. Figure 2 shows the details of these cells. Quartz spacers are used to position the electrodes. A thermocouple well is provided, as is a tube for attachment of the teflon tubing leading to the Hg/HgO/KOH reference electrode. A bulb is incorporated to collect gas for sampling, and a pressure transducer is attached to monitor this variable during the runs.



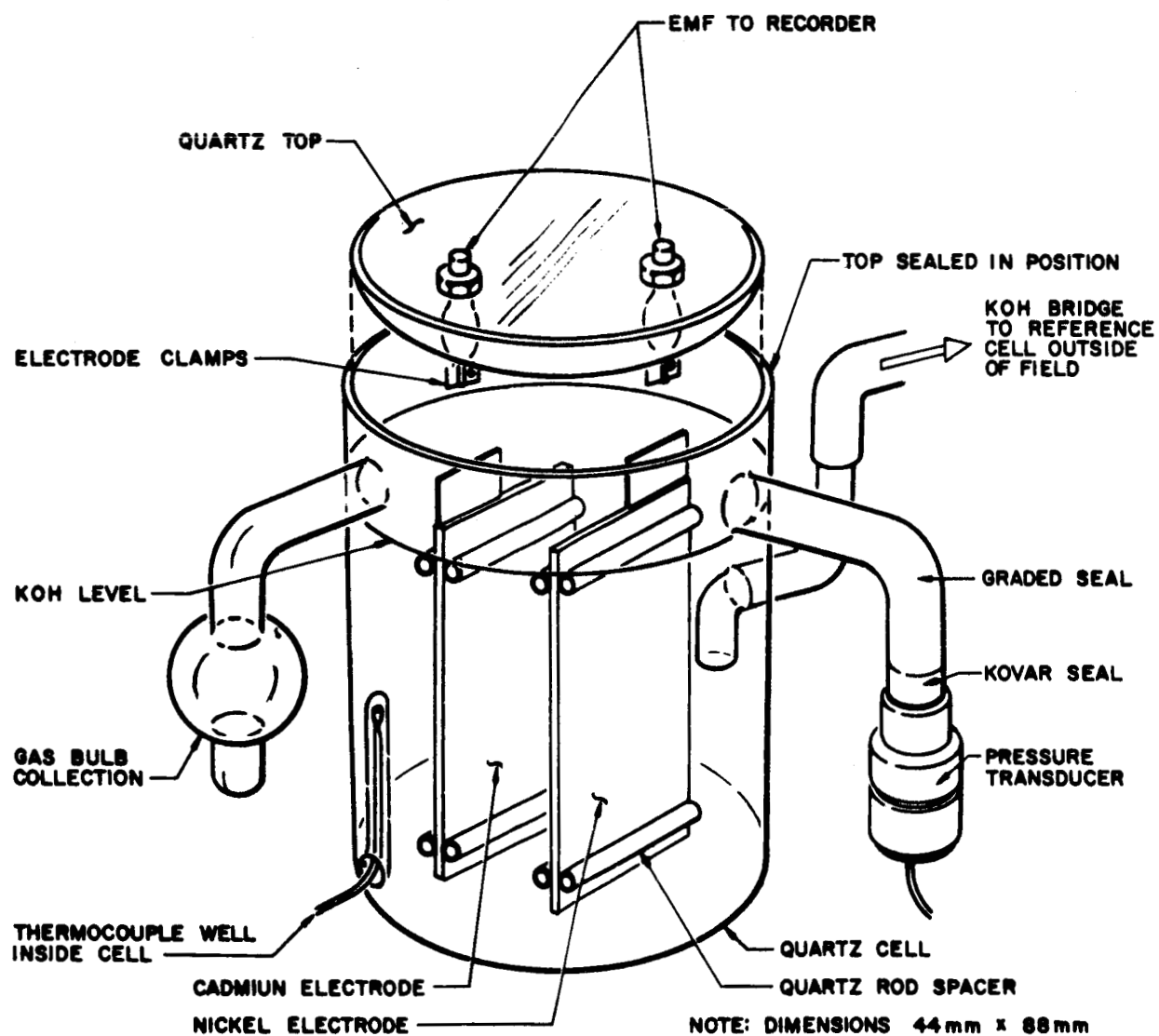


Figure 2. Quartz Cell for Irradiations.

One of the most troublesome questions in dealing with Ni-Cd batteries is knowing the state of charge of the battery. From the present work it became evident that a method for determining this variable would have to be derived. The electrodes used were obtained from Gulton VO type cells* of 0.8 amp hr rated capacity. These cells were selected as they were of flat plate design and were readily adaptable to our purpose. In these cells, which were plastic encased, are five electrodes, two of nickel and three of cadmium. In the laboratory cells one of nickel and one of cadmium are used.

A. Preliminary Tests

Various currents from 0.1 amp to 0.4 amp were tried for both charging and discharging. High currents were found to distort the electrodes and low currents were felt to be unrealistic. A current of 0.2 amp was selected. At first, cell voltage was thought to be the best indication of full charge but after further studies it was decided to charge all cells for 150 min at 0.2 amp. The capacity of the cells after the charge was $140 \text{ min} \times 0.2 \text{ amp} = 0.466 \text{ amp hr}$. After charging, the cells were discharged for 37 min to 75% of the total charge. It was found that another method of determining the state of charge of the cells was to use a Solion SV150 integrator in a series with the current sources. The color changes according to the charge and thus a visual indication of state of charge is obtained.

*Sintered plate type electrodes designed for sealed operation, manufactured by the Alkaline Battery Division of Gulton Industries, Inc.

Laboratory experiments were carried out in 30 and 40% KOH with no apparent differences. The following observations were made.

1. High currents (0.4 amp) distort the nickel electrodes whereas the cadmium electrodes seem unaffected. The curling does not appear to be directional. Hot spots occur with bulges appearing on the surface of the electrode.
2. Voltage across the Ni-Cd cell is not an indication of state of charge.
3. Upon charging, the cadmium electrode starts to gas when the cell has been charged with approximately the same number of coulombs which can be withdrawn on discharge.
4. Cells can be cycled in our system for 2-3 weeks with no apparent voltage changes anywhere in the cycle, but some residue has been noted falling from the cadmium electrode after rather long periods of operation (approximately 17 days).
5. Electrodes from the same battery behave similarly on cycling even to the extent that their voltages are the same within approximately 10 mv or so. Electrodes from different batteries show much greater differences.
6. No pressure changes were detected during cycling. A transducer sensitive to 0.1 psi was employed for these measurements.

B. Irradiation Tests

For the irradiation tests, a battery chosen at random is first charged according to the Gulton specification

(0.060 amp for 17 hrs). It is then dismantled and the electrodes placed in cells, one set for irradiation and the other as a control outside the field. The cells are not identical in construction but the electrode spacing is the same. After the hookup is complete, the cells are discharged and recharged at the 0.2 amp rate, discharged 25% and cycled, preparatory to the actual test in the radiation field.

Table I gives a summary of the runs accomplished. As the work must of necessity be exploratory, with so many possible variables, it appears of value to give an extensive discussion and evaluation of the results. These are presented below.

Runs No. 1 and 2 were essentially identical, except that the use of wolfram leads in Run No. 1 led to early failure and possible ambiguity in interpretation of the results. These runs showed the following:

1. A black precipitate was formed during the irradiation.
2. The cell emf (at all corresponding points in the cycle) dropped 70 mv in four hours of irradiation and then leveled out to retain this value 12 hours until failure.
3. The Ni vs Hg/HgO voltage dropped 60 mv in this time whereas the Cd vs Hg/HgO voltage dropped 10 mv.
4. The cell outside did not change over this period.
5. After the cell was lowered into the field, the polarization from open circuit to charge and from open circuit to discharge on the cycle decreased by 20 mv. (Possibly due to lowered electrolyte resistance and decreased activation polarization, if any.)

TABLE I

SUMMARY OF Co⁶⁰ IRRADIATIONS

Run No.	Co ⁶⁰ Source Used	Dose Rate (rads/hr)	Cell Type	Cell Temp, °C	Ref. Cell Temp, °C	Time, hrs	Integrated Dose Rate (rads)	Comments and Results
1	NAA Science Center	1.9x10 ⁶	Quartz	45	25	12	2.2x10 ⁷	Tungsten lead etched through. Sloughing off observed.
2	NAA Science Center	1.9x10 ⁶	Quartz	45	25	72	1.4x10 ⁸	SOEO*
3	NAA Science Center	1.9x10 ⁶	Quartz	45	45	62	1.2x10 ⁸	SOEO
4	NAA Science Center	1.9x10 ⁶	Quartz	45	none	5	9x10 ⁶	SOE observed in 3 hrs. Gassing observed.
4a	NAA Science Center	1.9x10 ⁶	Battery	45	none	7	1.6x10 ⁷	Separator impregnated with SOE material.
5	NAA Science Center	1.9x10 ⁶	Quartz	45	45	215	4x10 ⁸	System leaked and no press. meas. SOEO.
6	AI	8x10 ⁴	Lucite	26	none	96	7.7x10 ⁶	SOEO
7	AI	8x10 ⁴	Lucite	26	none	72	5.8x10 ⁶	Threshold for SOEO.
8	AI	8x10 ⁴	Lucite	26	none	168	1.3x10 ⁷	SOEO

*SOEO = Sloughing off of Electrode Occurred.

6. No pressure increase was detected (to 0.1 psi).

Data from work during the first two runs indicated that temperature effects on the Ni-Cd battery system had to be defined before electrochemical changes observed during irradiation could be attributed solely to the radiation. The experimental cell in the NAA Science Center Co⁶⁰ source operates at approximately 45°C. Preliminary temperature studies and early irradiation studies had indicated that the effects observed were not reversible in a reasonable length of time. To separate these effects, a run (No. 3) in the Co⁶⁰ source was carried out where the outside or reference cell would be thermostated at 45°C. so that differences observed would be entirely due to Co⁶⁰ radiation.

From the data from Run No. 3, it appeared that the voltage changes observed in Runs 1 and 2 were almost entirely due to temperature. Figures 3, 4, and 5 are typical curves from Run No. 3. (Note: First and last indicates point at start and finish of respective cycle.) The observation and conclusions from comparison of the results of these two runs can be summarized thus:

1. Radiation appears to cause a 10 mv shift in the open circuit voltage during the 62 hour irradiation period. Charge and discharge voltages appear to be affected to the same degree. This shift may grow larger with longer times. This point will be pursued further.
2. Three hours were needed to reach temperature equilibrium in the Co⁶⁰ cell. In Run No. 3, from the 16th to about the 28th hour of the run, the cell being irradiated was accidentally removed from the Co⁶⁰ source and was at room temperature. Note that upon being returned to room temperature the cell voltages did not return to their original value.

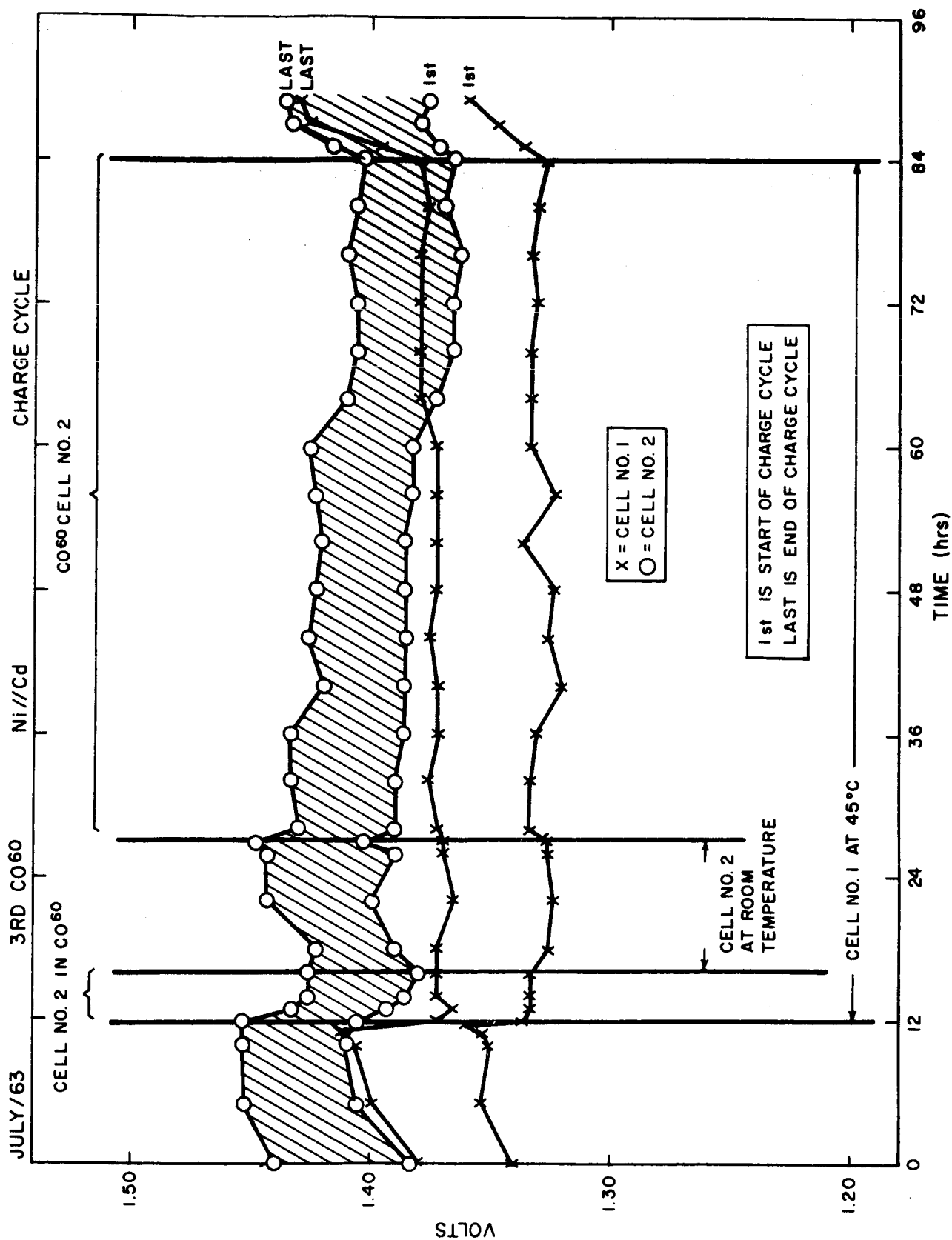


Figure 3. Nickel vs Cadmium on Charge Cycle.

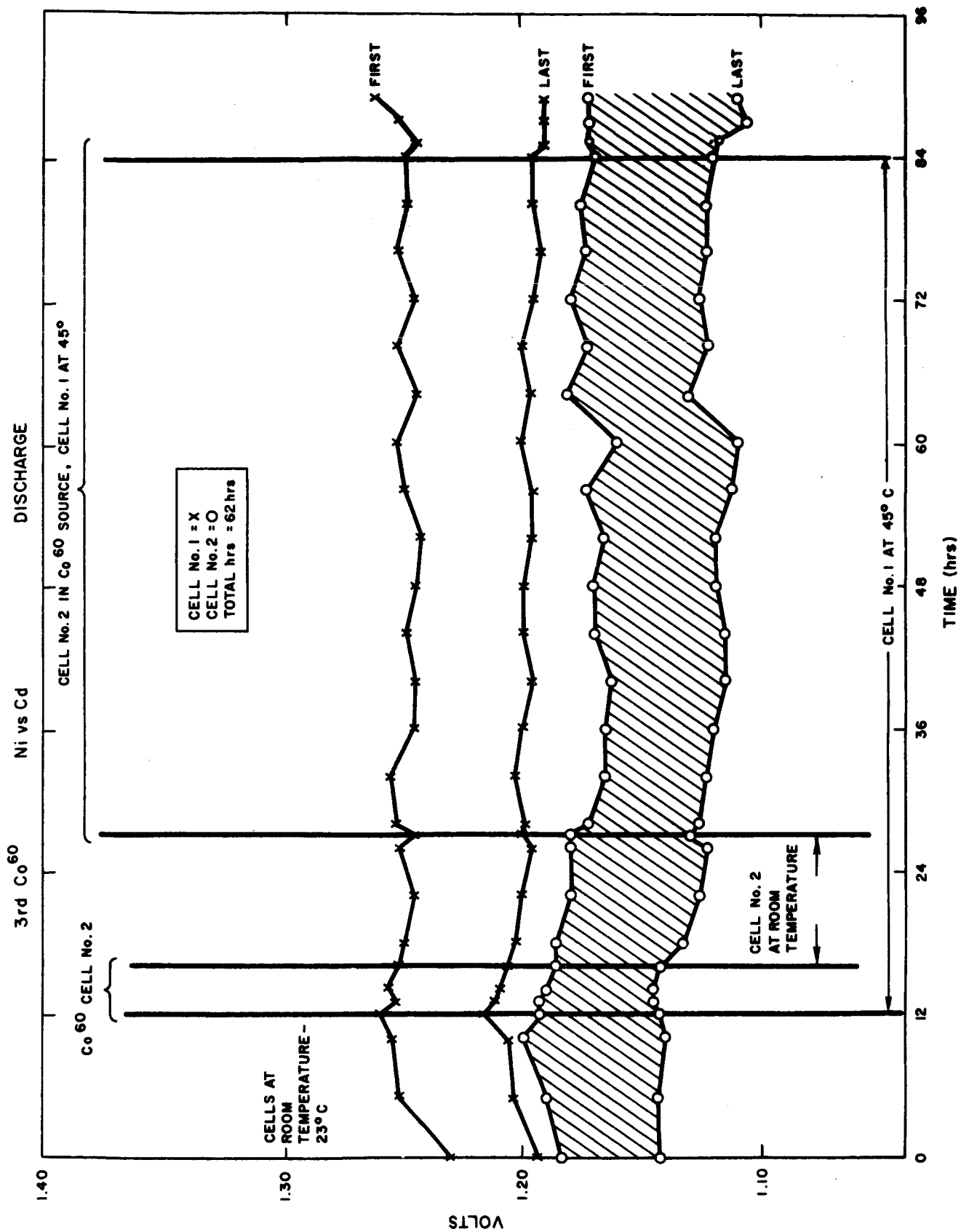


Figure 4. Nickel vs Cadmium on Discharge Cycle.

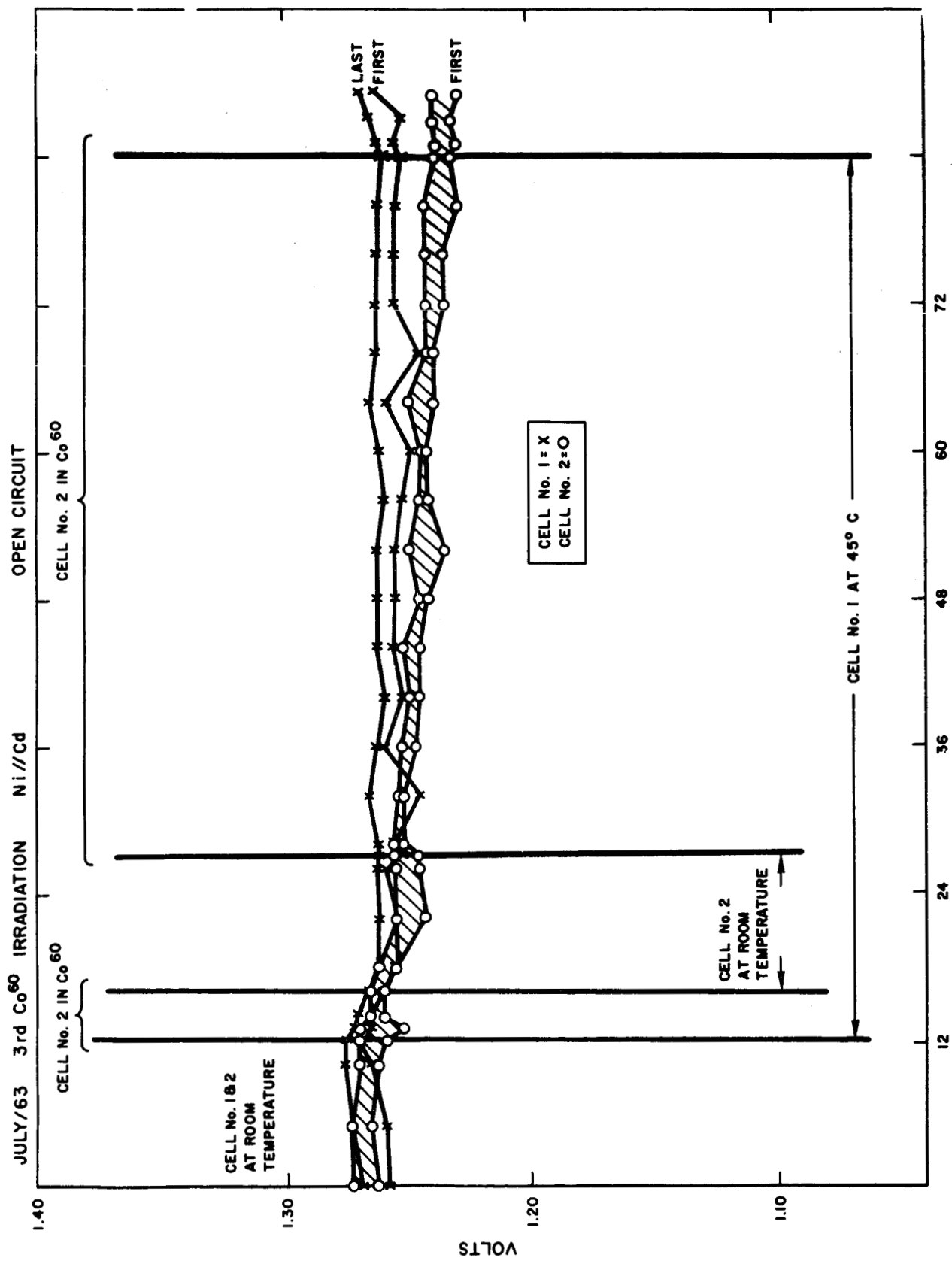


Figure 5. Nickel vs Cadmium on Open Circuit.

3. In Run No. 3, a break in the circuit to the reference electrode occurred during the Co^{60} irradiation. This condition was corrected late in the run. The cause was thought to be a bubble in the salt bridge connection.
4. Eleven milligrams of material which had sloughed off of the electrodes was collected from the irradiated cell in Run No. 3. (An average weight of a cadmium electrode is 5 grams.) Analysis of the sloughed material from this run is given in Table II, Col. 6. Analyses of such material from prior runs, as well as other analyses are given in Table II. The samples were:
- (1) Solids washed from cellulose battery separator.
 - (2) Sloughed-off residue from Co^{60} Run No. 1.
 - (3) Solids from filtrate of electrolyte of Co^{60} Run No. 2.
 - (4) Sloughed-off residue from Co^{60} Run No. 2.
 - (5) Sloughed-off residue from 17 day cycling of cell at room temperature.

A cadmium electrode was disassembled to give the skeleton weighing 0.9 gram and a powdered composite weighing 4 grams. These materials were analyzed, the results being given in Table III.

In accord with one aim of the project which is to determine the dose rate and dosage needed to initiate any effects, Run No. 4 was scheduled to determine the threshold for initiation of the "sloughing-off" phenomenon.

A quartz cell was prepared for a normal Co^{60} irradiation with the exception that the reference electrode was not hooked up and the cell was left on open circuit after

TABLE II

**EMISSION SPECTROGRAPHIC ANALYSES
OF VARIOUS POST-RUN SAMPLES**

Sample #	1	2	3	4	5	6
Ag	.5	.02	.05	.02	.3	.3
Al	.3	.3	.1	.4	.3	.3
B	.4	.03	.4	1	.1	.05
Ba	<.01	.3	<.01	<.01	.3	
Ca	.3	1	.03	.1	2	.1
Cd	.1	3	<.01	.1	>10	>10
Cr	.01	.01	.01	.05	1	.05
Cu	.2	.3	.01	.03	.3	5
Fe	.1	.1	.1	.2	.2	.2
Li	<.01	<.01	<.01	<.01	<.01	
Mg	.005	.02	.005	.005	.01	.05
Na	5	3	<.1	.5	.3	.2
Ni	.3	.05	<.01	.05	3	1
Pb	<.01	.1	<.01	<.01	.05	.5
Si	4	4	>10	>10	3	2
Sn	<.01	.05	<.01	<.01	<.01	.05
W	<.5	2	<.5	<.5	<.5	
Zr	<.05	<.05	.1	.5	<.05	.05

NOTE: Where a "<" value appears, element was not detected.

Values shown are in weight per cent.

TABLE III

CHEMICAL ANALYSES OF CADMIUM ELECTRODE

	<u>Analysis of Ni</u>	<u>Analysis of Cd</u>
Wt of Total Electrode 5.091 gms	29.2%	37.2%
Wt of an Electrode Skeleton 0.9040 gm	14.4%	---
Wt of Bulk Material 4.0481 gms	32.9%	37.9%

being charged and reduced to 75% of charge. The cell was placed in the Co⁶⁰ source for Run No. 4 and observed every 15 minutes for the first hour and then every hour thereafter. After 45 minutes, the electrolyte appeared cloudy but it was 5 hours before enough material was present to show up as a precipitate on the bottom of the cell.

During the same period as the above run, a complete battery at 75% charge was irradiated for a total of 7 hours and 24 min (Run 4a). The battery was disassembled and some black material was found on and in the separator. In addition, more material could be wiped off the cadmium electrode with a paper tissue. Little or none was found on the nickel electrode.

With this information now available, cells were built for irradiation in the AI Co⁶⁰ source where the dose rate was much lower. Because of cell size and shape, an

average dose rate of only 8×10^4 rads/hr was obtained. The cells (for Run No. 6, 7, and 8) were made of lucite which prevented the observation of cloudiness but did allow for observation of precipitate formation. At the dosage rate the precipitation occurred in 72 hours. There does seem to be a rough correlation of appearance of the process of material loss from the electrode with total dosage received. In both runs No. 4 and 7, the total dosage to the appearance of a significant amount of precipitate was approximately 6×10^6 rads.

A long term run (No. 5) was recently carried out. The aim here was to include gas pressure measurements and gas analysis as well as some quantitative measurement of the material sloughed off of the electrode. Also, the aim was to determine whether the amount of this precipitating material was proportional to the integrated dosage or not. Unfortunately, our cell was not leak proof (which, with our present design, is impossible to check before a run). In any case, we did not observe any pressure build-up and thus made no gas analysis over the 9 day run.

Analyses were completed of the cadmium and nickel electrodes. Spectrograph analyses were made on both electrodes and skeleton and quantitative analyses were made on cadmium electrode and its skeleton. The results are in Tables IV and III.

C. Temperature Characteristics of Ni-Cd Batteries

Different electrodes from battery cells give various results when cycled with temperature. The manufacturers of our cell (Gulton Industries) pointed out that the batteries have a memory. That is, their operating characteristics may be very dependent on their previous thermal

TABLE IV

SPECTROGRAPHIC ANALYSES OF CADMIUM
AND NICKEL ELECTRODES

	<u>Cadmium Electrode</u>	<u>Nickel Electrode</u>	<u>Electrode Skeleton</u>
Ag	.3	.1	T
Al	.5	--	T
Ba	--	.03	T
Ca	.3	.3	T
Cd	>10	.5	S
Co	--	2	T
Cr	.01	.1	S
Cu	.05	.05	T
Fe	.05	.1	M
Mg	.05	.05	T
Mn	--	--	S
Mo	--	--	T
Na	.8	.4	-
Ni	>10	>10	S
Pb	--	.05	T
Si	.2	.2	T
Sn	--	--	T
Zr	--	.1	T

Values shown are in weight per cent.

"M" indicates a major constituent

"S" indicates a minor constituent

"T" indicates a trace constituent

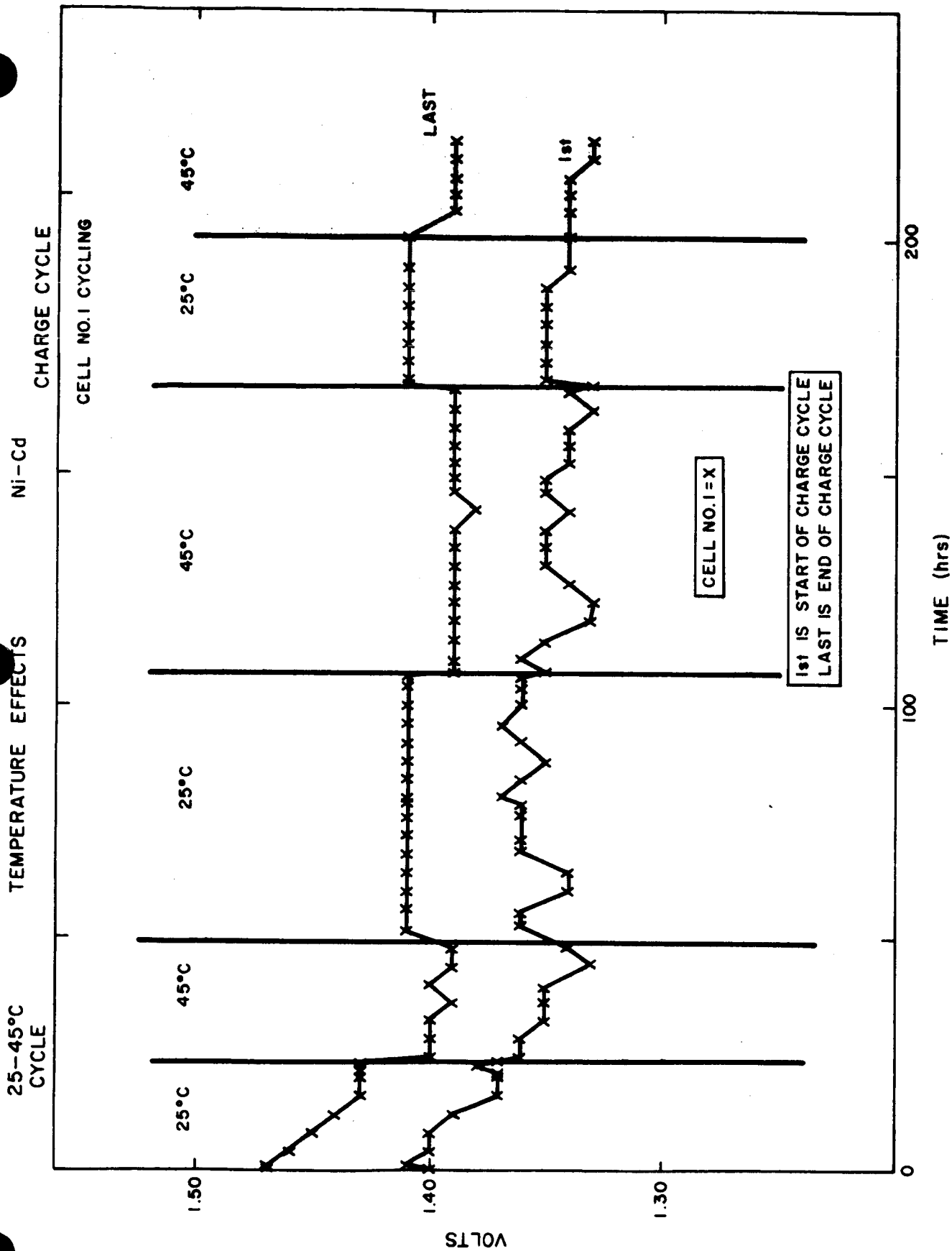


Figure 6. Temperature Cycling Results for Nickel vs Cadmium Cell Charge Cycle

history. Our first runs did not recover on excursions from 25 to 45°C and back to 25°C. A further run without radiation where the cycling was in five degree increments, e.g., 25-30-25-35-25 up to 45°C did recover. Additional study of this factor has been carried out. The results of this run are shown graphically in Figure 6. As is evident, in this cell at least there was a reversible change in cell behavior obtained with these temperature excursions.

Further information on the high temperature behavior and reversibility of these electrodes and cells has been solicited from the manufacturer (Gulton Industries, Inc.).

IV. DISCUSSION AND CONCLUSIONS

No immediate effects of radiation (gamma) at the dose rates employed were observed. This is not surprising, as the electrode reactions at the battery electrodes are fairly rapid (high exchange current density), as otherwise these electrodes would not be employed for this purpose. Thus, any H_2 or O_2 or H_2O_2 evolved during the radiation has no direct effect in establishing any electrode potentials.

The phenomenon of material sloughing off from the electrodes, almost entirely from the cadmium (negative) electrode, was unexpected. Its occurrence is predictable (now) and reproducible. While initial tests show its extent to be a function of integrated dose at different dose rates, this is only a tentative conclusion, subject to change as further data are gathered. One can anticipate the variation of this effect with quantity of water present, and with pH among other possible variables.

The following is a possible explanation of the cause of the disintegration of the cadmium electrode. Some hydrogen peroxide, gases, and free radicals are formed probably in and near both electrodes. In either electrode the gases from peroxide decomposition force their way out of the electrode. At the nickel electrode either because of a different pore structure or because the nickel-nickel oxide physical structure is strong, no material is sloughed. At the cadmium electrode, the cadmium metal or hydroxide is bonded to nickel, but probably not as strongly as is nickel in the nickel-nickel oxide case. The passage of the gas or peroxide either physically or chemically knocks cadmium off, together with the base porous nickel. Another possibility is that this gas is formed mostly in the cadmium electrode which may be a better catalyst for peroxide decomposition. This might explain the difference in the extent of the sloughing phenomenon observed. At present we have no reason to believe or disbelieve the latter explanation.

Eventually this material loss was found to affect the capacity of the cadmium electrode. Also, the change in voltage of cells under radiation treatment may be due to this effect.

The fact that some degree of material loss was observed with the commercial battery, and that some material penetrated the separator is of significance.

V. PLANS FOR FURTHER WORK

No gas evolution data have as yet been obtained, owing to a variety of unfortunate circumstances. A further run is planned with a modified cell at the NAA Science Center Co⁶⁰ source. The reference electrode will be incorporated into

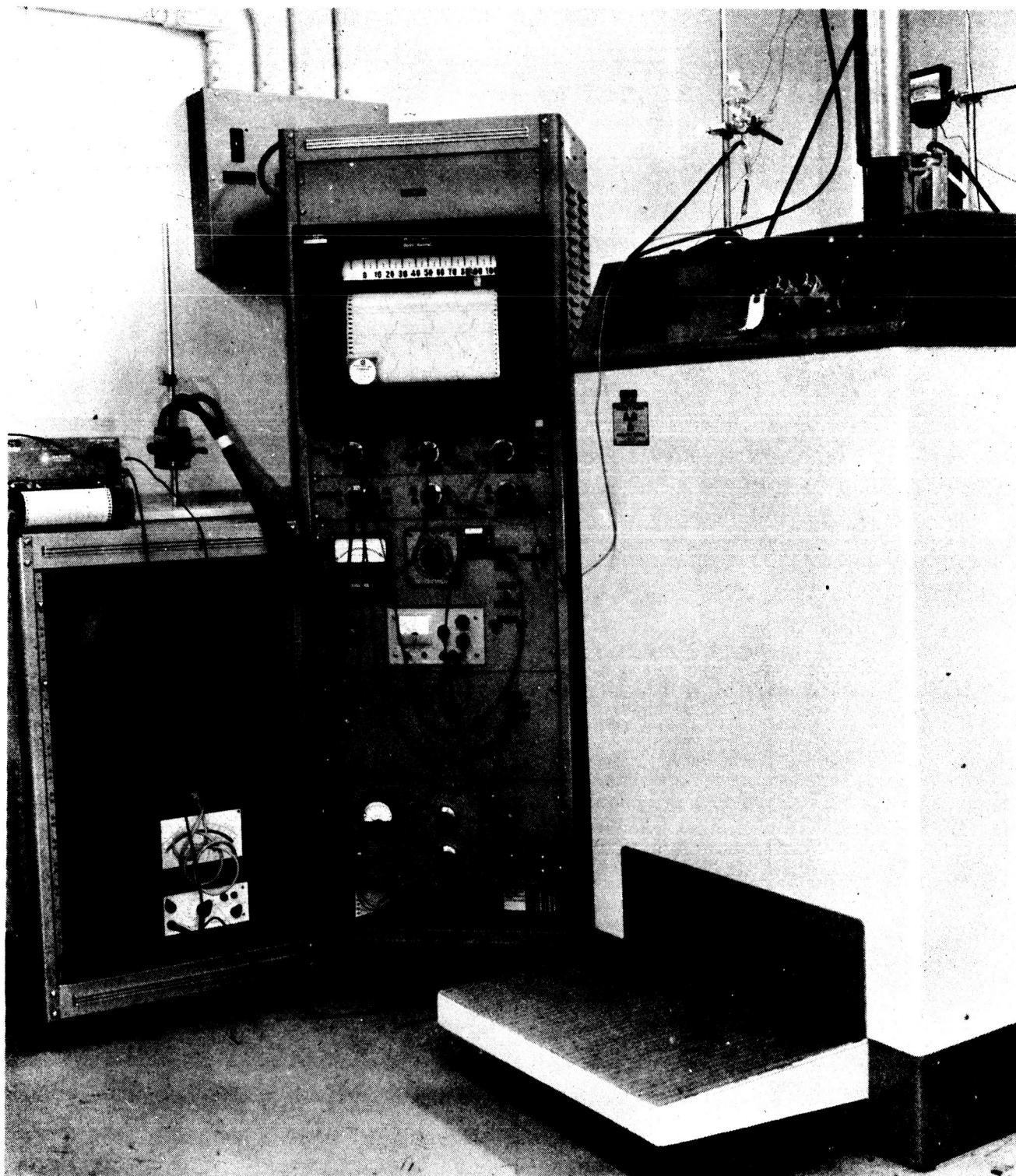


Figure 7. Test Cell Installed in NAA Science Center Co⁶⁰ Source.

the main body of the cell. This will enable us to seal the cell with no danger of leakage, so that gas samples and pressure build-up data will be obtained. Also, as we have much comparative data, we can determine the effect of this gamma radiation on the Hg/HgO/KOH reference electrode.

Tests with electron irradiation are planned, using a modified cell arrangement. This will enable us to get a better idea of the effect of very high dose rates and integrated doses on the extent and rate of the observed material loss.

Tests are planned outside of any radiation field on the effect of H_2O_2 on battery and electrode behavior. This may enable a decision to be made as to whether the peroxide or free radicals are the likely cause of the sloughing off phenomenon.

Arrangements have been worked out to use the SNAP shield test facility for neutron radiation studies. Unfortunately, the original estimate of the dose rate in this source was underestimated. If the results here are of the same type as obtained with gamma radiation, an equivalence factor of gamma and neutron may be worked out satisfactorily. If new phenomena are observed, or if more extensive neutron data are required, an outside source may be employed. This possibility is being planned for.


G. R. Argue
Specialist-Research


H. L. Recht
Supervisor-Electrochemistry

AI-8971
23


W. A. McCollum
Chemist